GEORGIA INSTITUTE OF TECHNOLOGY — OFFICE OF CONTRACT ADMINISTRATION

PROJECT ADMINISTRATION DATA SHEET

[x] ORIGINAL [ ] REVISION NO. _____

Project No. E-19-B07 — DATE 5/27/82

Project Director: Dr. M. Marek — School/Lab ChE

Sponsor: NIDR; PHS; DHHS

Type Agreement: Grant No. 5R01 DE03601-10

Award Period: From 7/1/82 To 6/30/~~83~~84 (Performance) 9/30/83 (if last year) (Reports)

Sponsor Amount: $30,157 direct costs (10th year) Contracted through:

Cost Sharing: $3,683 (E-19-323) 5% ~~GTRI~~/GIT

Title: Effect of Corrosion on Dental Amalgams

ADMINISTRATIVE DATA

OCA Contact: Linda H. Bowman x4820

1) Sponsor Technical Contact:

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2) Sponsor Admin/Contractual Matters:

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Defense Priority Rating: none

Security Classification: none

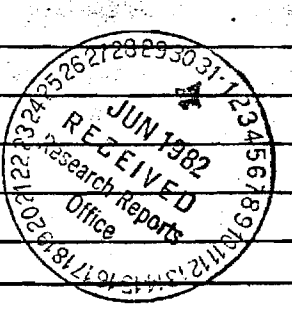
RESTRICTIONS

See Attached NIH Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval – Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with GIT, but none proposed.

COMMENTS:



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GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 11/9/84

Project No. E-19-B07 School/~~Lab~~ ChE

Includes Subproject No.(s) _____

Project Director(s) Dr. Marek ~~XXXXX~~ / GIT

Sponsor MDR;PHS;DHHS; National Institute of Dental Research

Title Effect of Corrosion on Dental Amalgams

Effective Completion Date: 6/30/84 (Performance) 9/30/84 (Reports)

Grant/Contract Closeout Actions Remaining:

- [X] None
- [ ] Final Invoice or Final Fiscal Report
- [ ] Closing Documents
- [ ] Final Report of Inventions
- [ ] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other _____

Continues Project No. _____ Continued by Project No. E-19-B08

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Project #: 6-19207

C. PROGRESS REPORT
7/1/79 through 8/31/82

Professional Personnel
Miroslav Marek, Ph.D., Associate Professor, 7/1/79 through 8/31/82, 40% (Principal Investigator).

NOTE: The 1979-82 research plan was prepared for the personnel of three: the PI and two Graduate Research Assistants (GRAs). Although funding as proposed was recommended, the budget was reduced as an austerity measure by deleting the funds for one of the GRAs. The PI was advised that a corresponding reduction in the effort was expected. Consequently, most of the work was performed by the PI and one GRA at one time. Therefore, some of the proposed program was reduced in scope. On the other hand, some additional work, not included in the proposal, was performed, including cooperative studies with other researchers. The principle used in the decisions concerning the emphasis, directions, and scope of the individual parts of the program was to reduce the effort where the remaining work was not expected to bring significant new findings (e.g., Specific Aim 3, reduction of the types of amalgam from four to one), or where the work was similar to the efforts in laboartories specializing in the area (e.g., some of the structural studies); to perform additional work when important knowledge could be efficiently gained because of the availability of prepared samples and experimental setups, or when a cooperation with other researchers has become possible. A table showing the comparison of the proposed and performed work is shown in Table 1.

Summary of Results

Specific Aims of the Previous Application

Specific Aim 1. To determine the mechanism of the corrosion effects in high-copper amalgams.

High-copper amalgam samples were corroded in 1% NaCl at constant potential (0.0 V, SCE); the solution was periodically analyzed for Cu, Sn, Ag, and Hg by Atomic Absorption Spectrophotometry (AAS); following the test period the samples were sectioned and analyzed by Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray Technique (EDAX).

Results: No Ag or Hg were detected in the solution. Sn concentration increased rapidly but stabilized at about 10^{-9} M. Solid corrosion products began to form on the surfaces of both the amalgam and the cell. Cu was detected in the electrolyte shortly after the beginning of the test but later than Sn. The concentration increased continuously during the test. Analysis of the structures showed copper depletion in the corroded layer. The η' (Cu-Sn) phase near the surface was converted into corrosion products of Sn with little Cu present. The products were nonmetallic but only Sn was detected (O and H could not be detected with EDAX), they were assumed to be tin oxide. Near the surface Cl was also detected in the products, which were assumed to be tin chloride hydroxide. Part of the matrix phase in the corroded layer was higher in Ag than γ_1; it was assumed to be β_1. A hypothesis was advanced (4) that tin dissolves from γ_1, destabilizes it, as suggested by Johnson (30), and γ_1 transforms into β_1.

A hypothesis also was made that the transport of Cu from η' to the surface is by diffusion in the matrix. Samples of γ_1 and β_1 phases were prepared, electroplated with copper, maintained at constant temperature, sectioned, and analyzed by electron microprobe. The diffusion parameters were determined. The results showed that copper diffused about two times faster in the β_1 than in the γ_1 phase. Thus the γ_1 - β_1 transformation may facilitate the transport and accelerate the corrosion process.

Table 1. Summary of the Work Proposed and Work Performed During the Past Project Period

WORK PROPOSED	WORK PERFORMED
1. Study of the Mechanism	
a. Corrosion tests-solution analysis	Performed
b. Tests of η'	Performed
c. Tests of multiple-phase electrodes	Performed
	Additional
	d. Study of Cu-diffusion in γ_1 and β_1.
2. Effect of Corrosion on Mechanical Properties	
a. Completion of mechanical tests	Performed (creep in coop. with MCG).
b. Metallography and x-ray	Performed but limited because of lack of significant new findings.
	Additional
	c. Joint with Univ. of Oregon: Relationship between Hg-content, creep and corrosion.
	d. Creep and corrosion of γ_1, β_1 as a function of Zn, Sn.
	e. Simultaneous corrosion and compressive creep.
	f. Simultaneous corrosion and tensile creep.
	g. Preliminary study of the effect of abrasion on creep.
3. Porosity vs. Corrosion	
a. Quantitative characterization of porosity	Performed
b. Corrosion tests	Performed
c. Analysis of the relationship	Performed
Same for three other amalgams	Deleted because of the cut in personnel.
4. Effect of Aging on Corrosion	
a. Corrosion tests	Performed
b. Limited structural analysis	Some performed but suspended because of cut in personnel.
5. Evaluation of Electrolytes	Performed
6. Evaluation of the Corrosion Test	Performed - in progress
	Additional
	7. A Study of Galvanic Interactions

DO NOT TYPE IN THIS SPACE—BINDING MARGIN

Samples of the η' (Cu_6Sn_5) phase were prepared by melting pure components in vacuum. The composition and structure were verified by microprobe and x-ray analyses. The corrosion properties were determined by measuring the potentiodynamic anodic polarization behavior, corrosion potentials, and potential differences between the η' phase and other phases of the amalgam microstructure. All tests were made in the following electrolytes: synthetic saliva, 1% NaCl (neutral), and 1% NaCl acidified to pH 1. The acidified solution was used to simulate conditions in occluded corrosion cells.

Results: In the nearly neutral synthetic saliva the η' phase suffered little deterioration; the anodic polarization curves showed no breakdown of passivity, and the corrosion potential differences between the phase and the γ and γ_1 phases were within 0.1 V. In 1% NaCl the activity of the η' phase increased but the corrosion rate remained relatively low in the range of potentials of interest. The highest activity was observed in the acidified solution; however, even in this case, the corrosion resistance was close to that of the other phases.

A joint study was made with Dr. T. Okabe and coworkers (MCG, Augusta, GA). Pure η' crystals were extracted from a binary Cu-Sn alloy and dispersed in various matrices, which included the γ_1 phase (Ag-Hg and Ag-Hg-Sn), pure Ag, and a mixture of γ_1 + unreacted alloy (commercial high-copper dental amalgam alloy). The susceptibility to corrosion was evaluated using constant potential coulometry. Some of the electrodes were examined in the SEM before and after the test. The results confirmed the high corrosion resistance of pure, isolated Cu_6Sn_5. There was no increase in susceptibility in the matrix of Ag. Susceptibility sharply increased in the matrix of Ag-Hg and Ag-Hg-Sn. The SEM examination showed that corrosion initiated at the interphase. The increase in corrosion susceptibility was attributed to the presence of Hg. This was confirmed in tests in which small amounts of mercury were plated on pure Cu_6Sn_5; a significant increase in the corrosion current density was observed. (Most of the samples were prepared at MCG; all tests and analyses were made at Georgia Tech.)

Summary of Conclusions

The results of this part of the program confirmed the basic phenomena of the mechanism of corrosion of high-Cu amalgams: deterioration of η', dissolution of Cu in the electrolyte. The explanation of the susceptibility of η' in the amalgam vs. pure η' answered one of the two major questions concerning the mechanism of corrosion and resolved the previous contradiction. The second major question concerns the transport of species from and to the electrolyte. The diffusion results for Cu did not prove that diffusion was the main transport mechanism for Cu or for other species.

The mechanism of deterioration of high-Cu amalgams is qualitatively understood with the exception of the transport phenomena within the structure. The mechanism of the effect of Hg on corrosion of η' needs to be better understood so that new alloys can be efficiently developed. Quantitative data for the depth of corrosion vs. time of exposure are lacking.

Publicizing of the results:

Publication I-c* in Treatise on Materials Science and Technology (~~in press~~).
(Deterioration of η', in amalgam, electrochemistry of pure η', γ_1 - β_1 hypothesis).
Paper II-a , submitted to the Journal of Biomedical Materials Research (Corrosion of η' in the matrix of γ_1). In press.
Presentation/Abstract V-i, IADR 1982 (Corrosion of η' in the matrix of γ_1).
Presentation/Abstract V-e, IADR 1980 (Diffusion of Cu in γ_1 and β_1).

*See the list of publications at the end of the Progress Report, and Appendix for copies.

Specific Aim 2. To determine the effects of corrosion on the mechanical properties of various types of dental amalgams. (The interdependence of mechanical and corrosion factors was investigated.)

In the first part of this study the determination of the compressive strength of 14 amalgams exposed to 1% NaCl for 2, 8, and 12 months was completed, (investigation started during the previous project period). The loss of strength was highest for low-Cu amalgams and reached as high as 50% for the 12-month exposure.

Although the results well demonstrated the severe effect of corrosion on mechanical properties, their usefulness was limited. Too many amalgams were tested to allow a more thorough study; the simple exposure conditions did not make it possible to relate the results to a definite electrochemical quantity; the use of 1% NaCl accelerated corrosion but prevented direct correlation with an oral exposure.

Many samples were examined by optical and SEM microscopy and X-ray techniques, and some of the results were reported in the publications listed at the end of this section. However, no truly significant new findings were obtained. The examination of the fracture path was deleted because of the personnel reduction.

A joint study was made with D. Mahler and coworkers (University of Oregon) on the effects of the final mercury content on both creep and corrosion. Two different coulometric tests were used for the evaluation of the corrosion susceptibility. Both creep and corrosion increased sharply when a critical Hg content was exceeded. The effect was attributed to the increasing Sn content in γ_1.

(The preparation of the specimens, the creep tests, and one type of the corrosion tests were made at the UO; the second corrosion test was made at GaT. Results were analyzed in discussions between the investigators.)

A joint study was made with M.B.Butts and coworkers (MCG) on creep of corroded high-Cu amalgam. Corroded specimens showed lower creep values than controls. The effect was tentatively attributed to the $\gamma_1 - \beta_1$ transformation enhanced by corrosion.

(Specimens were prepared and creep tested at MCG, corroded at GT.)

A study was made of creep and corrosion of the γ_1 and β_1 phases as a function of Sn and Zn content. The samples were prepared by trituration of powders with mercury (first phase) and by melting, followed by pulverizing and pressing (second phase). Corrosion was evaluated by constant potential coulometry.

Results, First Phase: β_1 showed lower creep than γ_1. Sn sharply increased creep of γ_1 and less drastically of β_1. Zn decreased creep of γ_1 and had little effect on β_1.

Results, Second Phase: Small amounts of Sn decreased the grain size of γ_1. When the creep results were corrected for the effect of grain size, Sn still significantly increased creep rate of γ_1; the effect on β_1 was not significant. Both Sn and Zn made the phases electrochemically more active.

Tests of simultaneous corrosion and compressive creep showed little effect of creep on the corrosion rate. A study was made of the effect of tensile stress and strain. A constant load pneumatic tensile machine was adapted for the tests; dumbbell-shaped amalgam specimens were placed in a temperature-controlled cell which also contained a reference and counter electrodes. The electrolyte was synthetic saliva at 37°C. Tests were made at various tensile loads. Five commercial amalgams, representing all the major types, were included in the study. The polarization resistance, which is inversely proportional to the corrosion rate, was determined using a transient polarization technique for various stress levels. Anodic polarization curves were recorded for unstressed and stressed conditions (18 MPa).

Results: Stressed specimens showed substantially higher passive current density in the polarization tests, especially the low-Cu amalgams. The breakdown potential was not affected. Polarization resistance showed a decrease (increased corrosion rate) for low-Cu amalgams at high stresses. The effects were attributed to the fracture of passive films by plastic strain.

Amalgam specimens exposed in flanges of dentures worn by human patients were examined in a joint study with S. Reese (Emory University). After 14 months of exposure there was no detectable corrosion of samples of high-Cu amalgams representing the major types of alloys. Low-Cu amalgams also showed much lower corrosion than retrieved restorations; particles of uncorroded γ_2 phase being found as close as 10 μm from the exposed surface.

(Preparation of samples and dentures, as well as monitoring of the patients, was performed at Emory University. Retrieved samples were analyzed at Ga T).

A preliminary study was made of the effects of abrasion on the corrosion of five types of dental amalgam. Potential-time and anodic polarization curves were recorded. The results have shown a substantial acceleration of corrosion even by relatively mild abrasion, and slow repassivation of abraded surfaces, indicating that during mastication the protection against corrosion is greatly reduced.

Summary of Conclusions: The creep and corrosion vs. Hg content results showed that creep and corrosion can be similarly affected by microstructural changes; therefore, creep values can indicate the conditions causing susceptibility to marginal fracture but creep does not necessarily cause the fracture. The creep and corrosion data as a function of Sn substantiated the creep-corrosion relationship; the effect of Zn on creep showed that creep and Zn, which are both used as parameters in the Mahler's model (21), are not independent. The lower creep of β_1 vs. γ_1 is in agreement with the interpretation of the results of the creep tests of corroded amalgams, but other effects also may be responsible (e.g., corrosion products within the structure). The acceleration of corrosion by tensile stresses and abrasion shows that corrosion of the occlusal surfaces of the restorations may be accelerated by mechanical forces, especially near the margins. The decisive role of mechanical forces in corrosion of occlusal surfaces was confirmed by the absence of corrosion effects in vivo, in the absence of masticatory forces.

Publicizing of the Results:

Publication I-b in the Journal of Dental Research (Creep and Corrosion).
Paper III-b, submitted to the Journal of the ADA (Corrosion in vivo in the Absence of Mechanical Forces).
Paper II-c, submitted to the Journal of Dental Research. (Effect of Tensile Strain on Corrosion). In press.
Thesis IV-b, Averette, Ph.D., 1982 (Corrosion vs. Strength, Creep and Corrosion of Matrix Phases, Effect of Tensile Strain on Corrosion).
Presentation/Abstract V-c, IADR 1980 (Creep of Matrix Phases).
Presentation/Abstract V-a, IADR 1979 (Corrosion vs. Hg Content)
Presentation/Abstract V-j, IADR 1982 (Effect of Creep on Corrosion).

Presentation/Abstract V-k, AADR 1983 (Corrosion of dental amalgam in vivo)
Presentation/Abstract V-l, AADR 1983 (Effect of abrasion on corrosion).
Paper III-a, submitted to the Journal of Dental Research (Acceleration of Corrosion by Abrasion).

Specific Aim 3. To determine the relationship between porosity, mercury content, and corrosion of dental amalgam.

A thorough study of the porosity and its effect on the corrosion behavior was performed. The study was made for a high-copper, single composition alloy (Aristalloy CR) which shows relatively high corrosion activity. The samples were prepared at different initial Hg/alloy ratios but at nearly constant final Hg content. The porosity was evaluated by metallography, gas adsorption analysis, and vacuum impregnation with liquids. The evaluation included determination of the number of pores in various size classes, determination of the form factor, and calculation of the true surface area, which included the surface area of the open pores. Corrosion tests were made in 1% NaCl by the coulometric constant-potential method. Tests were also made on samples impregnated with epoxy resin which filled the pores.

The results showed that the porosity increased with decreasing Hg/alloy ratio. The true surface area of a specimen of a nominal 1 cm^2 area increased from 2.99 cm^2 for 54% Hg to 3.99 cm^2 at 50% Hg to 6.64 cm^2 for 46% Hg (initial mercury contents). The corrosion index, obtained from the coulometric tests, increased linearly with the true surface area. Tests with epoxy-impregnated specimens showed lower corrosion index and corrosion depth after epoxy- impregnation.

The structure of the amalgam in the vicinity of the pores was examined using SEM and EDAX. The phases observed on the internal surfaces of the pores were then metallurgically duplicated, assembled in galvanic cells simulating the cells in the pores, and the corrosion potentials and currents were measured.

The results showed that the acidification of the solution in the pores, which results from the corrosion processes, made the Cu_6Sn_5 more susceptible to the attack; the γ_1 phase containing tin also showed anodic activity. This study was performed before the results of the study on the effect of mercury on the corrosion of Cu_6Sn_5 were known; therefore, the effect of mercury was not taken into account.

Because of the reduction in personnel and the very through study performed only one type of amalgam was examined instead of the four in the proposed research plan.

Summary of Conclusions: All dental amalgams are substantially porous. The results of this study point up that reduction of porosity by changes in mercury/alloy ratio, size of powder particles, trituration variables, etc. would be basically beneficial with respect to corrosion. The accelerating effect of porosity is important also in the examination of the causes of breakdown of margins because the marginal areas are often more porous than the bulk of the restoration.

Publicizing of the Results:
Thesis IV-a, (P. Biltoft, M.S.), 1981.
Presentation/Abstract V-h, IADR 1981.
Manuscript in preparation

Specific Aim 4: To determine the effects of aging on the corrosion behavior

The corrosion behavior as a function of the aging time was examined for the dispersed phase amalgam (Dispersalloy), which contains about 12% Cu in the alloy, and for a very high-copper amalgam (Sybraloy), which contains about 30% Cu in the alloy and in which no γ_2 phase can be detected even initially. The corrosion tests were made using the constant potential coulometry. The aging times ranged from one day to two months. The results have confirmed the previously reported change in the corrosion susceptibility of Dispersalloy with aging attributed to elimination of small amounts of γ_2 (55). However, the very high-copper amalgam which has no γ_2 showed even stronger influence of aging on corrosion. The corrosion index (total anodic charge in 24 hours) for

Dispersalloy changed from 9.9C to 8.0C (mean values) for aging time one day and two months. For Sybraloy the mean values were 12.3C and 6.4C. A metallographic and x-ray examination of the structure of Sybraloy as a function of aging so far has not revealed the cause of the change in corrosion susceptibility.

Further efforts in this direction have been suspended (at least temporarily) because the microstructural changes associated with aging have been studied in other laboratories, which specialize in structural studies (e.g., Marshall & Marshall, Northwestern University).

Publicizing of the results: None to date.

Specific Aim 5. To evaluate the electrolytes used in the in vitro corrosion tests of dental amalgam.

Seven synthetic electrolytes, which have been reported in the literature as substitutes for the oral environment in corrosion tests, have been examined. These included five synthetic salivas (31, 32, 33, 34, 35), Ringer's Solution (36), and modified Ringer's Solution (37). The Redox potential, pH, and buffering capacity were measured for each electrolyte. The results showed that, generally, only synthetic salivas which contain bicarbonates and CO_2 approximate human saliva in the buffering capacity, which is important in the corrosion processes.

Anodic polarization curves were recorded for a low-Cu amalgam in each of the electrolytes as well as in human saliva. The results showed that all five synthetic salivas produced results closely approximating those obtained in human saliva. Substantially different results were obtained with both types of Ringer's solution because of the high chloride concentration.

Summary of Conclusions: In in vitro tests which are to simulate closely in vivo conditions, the use of synthetic oral environment is mandatory. For long-term exposures the buffering capacity of the electrolyte should be close to that of human saliva. Electrolytes high in chloride concentration are appropriate only for accelerated tests in which the evaluation is strictly on a relative basis.

Publicizing of the results:

Publication I-c in Treatise on Materials Science and Technology (~~in press~~). (Table of electrolytes, anodic polarization curves).

Specific Aim 6. To evaluate the corrosion test for dental amalgam based on controlled potential coulometry.

The corrosion test based on constant potential coulometry, developed during the previous project period, was used in several parts of the project. In the reported program period measurements were made to determine if pure γ_1 (Ag-Hg, without Sn) is attacked during the test at 0.0 V (SCE). An attack would signify that the potential is too high for measurements relevant to in vivo conditions. No attack, however, was recorded in the 24 hour period of the test.

A study was made to compare various corrosion tests with the results of the measurements of the corrosion depth of specimens exposed for one year to 1% NaCl at 37°C. The other tests included weight loss, corrosion potential, passive current density, and polarization resistance measurements. The results of the constant potential coulometric test showed best agreement with the relative depth of corrosion.

All the test data for various amalgams have been saved for a statistical analysis to be performed at the end of the project period. The latest tests involve long-term exposures (250 hours); the results to date show that there are substantial differences between the different high-cu amalgams in long-term test results even if there are small differences in the 24 hour results. The corroded specimens are collected for structural analysis. Because of the long exposures the study progresses slowly and will continue to the end of the project period, which has been extended to 6/30/84.

Publicizing of the Results:
Publication in Journal of Dental Research, 1980.
Presentation/Abstract V-b, Biomaterials Symposium, 1979 (Comparison of Results of Various Corrosion Tests with Relative Depth of Corrosion in vitro).
Several major manufacturers of alloys for dental amalgam use the test to evaluate new alloys.

Specific Aim Added during the Project Period: A study of the galvanic interactions between dental amalgam and other restorative materials.

This study was conducted in addition to the planned program in view of the important galvanic effects observed in the previous part of the project. In one part of the study the interaction between metals which are not in contact was analyzed theoretically and examined experimentally. In the second part the interactions between metals in contact were measured using two dental amalgams (conventional and high copper) and dental casting alloys which included high-gold, low-gold, silver-palladium, and base-metal alloys. The numerical index of the galvanic effect was obtained by integrating the galvanic current for 24 hours.

Summary of conclusions: 1. There is no significant interaction between dissimilar metals in the mouth which are not in contact; 2. There is a substantial concentration macrocell due to the difference between saliva and the tissue fluids, which may have an important effect on the corrosion of the part of the restoration within the tooth cavity; 3. The measurement of open circuit potential differences between various dental materials is of little value in predicting the intensity of the galvanic interactions. The kinetics of reactions on both the anode and the cathode must be known to predict the interaction. Alloys which are efficient cathodes, such as silver-palladium casting alloys, cause stronger acceleration of corrosion of amalgams than, for instance, gold alloys which are relatively poor cathodes, in spite of the potential differences which point in the opposite direction.

Publicizing of the Results:
Publication II-a, in Treatise on Materials Science and Technology (in press) (Analysis of the Galvanic Interaction, Results).
Presentation/Abstract V-d, AADR 1980.

INVENTIONS

A record of invention "Cavity Liner for Sealing and Protection of Dental Restoration" has been registered by the PI (ROI 786 NCS). The subject is related to this research program but not directly part of it.

Publications Since the Last Competitive Review

10/1/78 - Present

I. Published Papers (Reprints in the Appendix)

a. M. Marek, "Corrosion Test for Dental Amalgam," Journal of Dental Research, 59, 63 (1980).

b. D. B. Mahler, J. D. Adey, and M. Marek, "Creep and Corrosion of Amalgam," Journal of Dental Research, 61, 33 (1982).

M. Marek: "Corrosion of Dental Materials" in "Aqueous Corrosion and Passive Films," Treatise on Materials Science and Technology, (J. C. Scully, ~~and J. Castle,~~ Editors), pp. 331-394, Academic Press, Vol.23, 1983.

The Chapter contains not only a review of the published literature on corrosion of dental materials up to 1980, but also most of the previously unpublished work of the Principal Investigator including the results of this project.

II. In Press (Copies of proofs or manuscript in the Appendix)

a. M. Marek, T. Okabe, M. B. Butts, and C. W. Fairhurst, "Corrosion of the η' (Cu-Sn) Phase in Dental Amalgam," Journal of Biomedical Materials Research.

b. M. Marek: "Corrosion of Dental Materials," in Encyclopedia of Materials Science and Engineering, (M. B. Bever, Editor) Pergamon Press.

c. D. F. Averette and M. Marek, "The Effect of Tensile Strain on Corrosion of Dental Amalgam," Journal of Dental Research.

III. Papers Submitted (Copies of the manuscripts in the Appendix)

a. M. Marek, "Acceleration of Corrosion of Dental Amalgam by Abrasion," (Journal of Dental Research).

b. S. B. Reese, D. Warfield, and M. Marek, "In Vivo Corrosion of Dental Amalgam in the Absence of Masticatory Forces," Journal of the ADA.

Rejected as more suitable for a research-oriented publication. Now being revised.

IV. M. S. and Ph.D. Theses (Copies of the Abstracts in the Appendix)

a. P. Biltoft: "The Effect of Porosity on the Corrosion of Dental Amalgam." (M. Marek, thesis director). M.S., Georgia Institute of Technology, Atlanta, GA, June, 1981.

b. D. F. Averette: "The Relationship Between Corrosion and Mechanical Properties of Dental Amalgam." (M. Marek, thesis director). Ph.D., Georgia Institute of Technology, Atlanta, GA, June, 1982.

V. Abstracts, Presentations, and DMG/IADR Microfilm Papers

a. M. Marek and D. Mahler: "The Corrosion Susceptibility of a High-Copper Amalgam as a Function of the Mercury Content," 57th Session of the IADR, New Orleans, LA, 1979, DMG/IADR 1979 Microfilm, Paper No. 968.

b. M. Marek: "In Vitro Measurement of the Corrosion Resistance of Dental Amalgam," 11th International Biomaterials Symposium, Clemson, S.C., 1979.

c. D. F. Averette and M. Marek: "Creep of the Matrix Phases of Dental Amalgam as a Function of Composition," Annual Session of the AADR, March 20-23, 1980, Los Angeles, CA., DMG/IADR 1980 Microfilm, Paper No. 105.

d. M. Marek: "Galvanic Interactions Between Dental Amalgam and Other Restorative Materials," Annual Session of the American Association for Dental Research, March 20-23, 1980, Los Angeles, CA., DMG/IADR 1980 Microfilm, Paper No. 1033.

e. S. B. Reese, R. F. Hochman, and M. Marek: "Low Temperature Diffusion of Copper in the α_1 and β_1 Phases of Dental Amalgam," Annual Session of the AADR, March 20-23, 1980, Los Angeles, CA., DMG/IADR 1980 Microfilm, Paper No. 106.

f. P. M. Soni, R. F. Hochman, and M. Marek: "The Effect of Fluoride on the Corrosion Behavior of Dental Amalgam," Annual Session of the AADR, March 20-23, 1980, Los Angeles, CA., DMG/IADR 1980 Microfilm, Paper No. 809.

g. M. B. Butts, T. Okabe, R. J. Mitchell, M. Marek, and C. W. Fairhurst: "Creep of a Corroded High-Copper Amalgam," Annual Session of the AADR, March 20-23, 1980, Los Angeles, CA., DMG/IADR 1980 Microfilm, Paper No. 282.

h. P. Biltoft, R. F. Hochman, and M. Marek: "The Effect of Porosity on Corrosion of Dental Amalgam," 1981 Annual Meeting of the IADR/AADR, March 19-22, Chicago, Illinois, DMG/IADR 1981 Microfilm, Paper No. 387.

i. M. Marek, T. Okabe, M. B. Butts, and C. W. Fairhurst: "Corrosion of the η' (Cu-Sn) Phase in Dental Amalgam," 1982 Meeting of the IADR, March 17-21, New Orleans, LA., DMG/IADR Microfilm, Paper No. 448.

j. D. Averette and M. Marek: "The Effect of Creep Deformation on Corrosion of Dental Amalgam," 1982 Meeting of the IADR, March 17-21, New Orleans, LA., DMG/IADR Microfilm, Paper No. 449.

k. S.B. Reese, D. Warfield, and M. Marek: "In vivo Corrosion of Dental Amalgam," 1983 Meeting of the AADR, March 17-20, Cincinnati, OH, DMG/AADR Microfilm, Paper No. 180.

l. M. Marek: "Acceleration of Corrosion of Dental Amalgam by Abrasion," 1983 Meeting of the AADR, March 17-20, Cincinnati, OH, DMG/AADR Microfilm, Paper No. 179.

D. METHODS

Some of the methods to be used in the proposed program are the same as those that have been used with good results in the previous programs. Potentiostatic and potentiokinetic measurements are made using a Wenking Model 70 TS 1 electronic potentiostat with a scan generator, potential meter, logarithmic converter, and X-Y recorder; the test solution is usually synthetic saliva (31) at 37°C, stirred and maintained at pH 6.7 by bubbling through it a mixture of either nitrogen or air with 10% CO_2. Coulometric tests are made at constant potential; the anodic current is electronically integrated (Wenking Integrator Model) to obtain total anodic charge per unit area. The anodic charge is directly proportional to the mass of the metal converted into corrosion products (dissolved ions or solid nonmetallic compounds) and is a good measure of the extent of the corrosion damage. Depending on the purpose, the test is made either in 1% NaCl or in synthetic saliva.

The electrode and fracture surfaces are examined by optical microscopy and scanning electron microscopy (SEM: Cambridge Mark II or Model 150 Stereoscan). Energy-dispersive x-ray analysis in the SEM or an electron microprobe are used to identify the phases present. Optical metallography and SEM examination of polished cross sections are used to determine the depth of the corroded layer.

The more specialized techniques and the procedures which are planned to be used to accomplish each Specific Aim are briefly described below.

1. Mechanism of Corrosion of γ_2-free Dental Amalgam

1a. Investigation of the Electrochemical Stability of the Intermetallic Phases in the Presence of Mercury

The effect of Hg on the stability of the passive films on Cu_6Sn_5 and Cu_3Sn will be further studied to gain a better understanding of the mechanism (continuation of the current work, see Progress Report). Mercury will be plated in various amounts on pure